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# Influence of $H_2O$ and $CO_2$ on the selective CO oxidation in $H_2$-rich gases over Au/$\alpha$-$Fe_2O_3$

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**Abstract**

The effects of $CO_2$ and $H_2O$ on the preferential CO oxidation in $H_2$-rich gases (PROX) over Au/$\alpha$-$Fe_2O_3$ have been studied by kinetic and IR spectroscopic measurements at 80 °C. Addition of $CO_2$ reduces the CO oxidation rate and the selectivity, which based on a blue shift of the linearly adsorbed CO in the IR spectra is attributed to coadsorption of $CO_2$ on the gold particles or at the gold–metal oxide interface. Furthermore, deactivation is accelerated due to increased carbonate formation on the catalyst surface. Addition of $H_2O$ results in opposite effects. It increases the selectivity by suppressing the competing $H_2$ oxidation reaction. The CO oxidation rate is slightly accelerated. The deactivation is significantly diminished, which is ascribed to the transformation of surface carbonates into thermally less stable bicarbonate species. The extent of the effect of water addition depends strongly on the reaction temperature, being most pronounced at lower temperatures (40 °C). Under realistic conditions (25% $CO_2$, 10–15% $H_2O$, 80 °C) water reduces, but cannot completely compensate, the negative influence of $CO_2$ on the PROX performance compared to $CO_2$-free gas mixtures.

*Keywords:* Selective CO oxidation; PROX; Gold catalysts; Au/$Fe_2O_3$; $CO_2$ effects; $H_2O$ effects; Carbonate formation; Deactivation; CO adsorption; DRIFTS; Kinetics

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## 1. Introduction

Supported gold catalysts are well known to be highly active already at low temperatures in several oxidation reactions, among them the oxidation of carbon monoxide at low temperatures. Comprehensive review articles are provided, for example, in Refs. [1–4]. One major application could be the selective oxidation of CO in $H_2$-rich gases (preferential oxidation of carbon monoxide—PROX), which is currently the most attractive method for the removal of CO impurities (ca. 1–2%) from feed-gas streams for polymer electrolyte fuel cells (PEFCs) produced by steam reforming of alcohols or hydrocarbons (see, e.g., Refs. [5,6]).

So far, most studies on the selective CO oxidation over gold catalysts have been conducted in model atmospheres (“idealized reformate”), consisting of CO, $O_2$, $H_2$, and an inert component ($N_2$ or He) [7–17]. Realistic methanol steam reformate, however, contains up to 25% $CO_2$ and 10–15% water. Therefore, it is essential to investigate the influence of these possible coreactants on the PROX reaction in order to evaluate whether the high activity and selectivity observed in idealized reformate are also maintained under more realistic conditions. For platinum-based catalysts, where due to the high adsorption energy of CO the active metal is “shielded” by a dense CO adlayer under typical reaction conditions, the presence of $CO_2$ and/or water was found to have rather small, “indirect” effects, caused by adsorption on the support [18,19]. In contrast, on supported gold catalysts the rather low CO adsorption energy and consequently lower steady-state CO coverage [10,20] may allow significant coadsorption on the metal surface, which in turn may result in much more severe effects. This is the topic of the present study, where we investigated the effects of $CO_2$,

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$H_2O$, and $CO_2/H_2O$ addition on the PROX reaction over a number of slightly different Au/$\alpha$-$Fe_2O_3$ catalysts at a representative reaction temperature of 80 °C.

The results of previous studies on this topic, which have not yet led to a consistent picture, can be summarized as follows. The influence of water addition on the CO oxidation reaction over supported gold catalysts, in the absence of $H_2$ or $CO_2$, had been investigated in several studies. The results, however, differ significantly, even on similarly prepared catalysts and for the same support material. Positive effects were reported by several authors for a variety of support materials. For instance, the activity of a Au/$\alpha$-$Fe_2O_3$ catalyst (1 kPa CO in air; 30 °C) was reported to increase from 95% conversion to total conversion upon the addition of 0.6–4 kPa water [21]. Positive effects were also claimed for Au/$TiO_2$, Au/$Co_3O_4$, Au/NiO, or Au/$Al_2O_3$ catalysts [1,22–25]. In contrast, Daté and co-workers reported recently that only small concentrations of moisture (200 ppm) were beneficial for the CO oxidation over a Au/$TiO_2$ catalyst (1 kPa CO in air; 0 °C), while larger concentrations decreased the activity [26,27]. Since the water–gas-shift activity of Au/$TiO_2$ is negligible at these low temperatures [28], the enhanced reactivity cannot result from the water–gas-shift reaction ($H_2O + CO \leftrightarrow H_2 + CO_2$). In contrast to the above studies, Bollinger and Vannice claimed an irreversible decrease of the activity by a factor of 3 for a Au/$TiO_2$ catalyst upon addition of 0.6 kPa $H_2O$ (4.8 kPa CO and $O_2$; 40 °C) [29]. Similar observations were made by Grunwaldt et al., who reported a reduced activity over Au/$TiO_2$ (0.25 kPa CO and $O_2$; 30 °C) with only 0.1 kPa $H_2O$ present in the reaction atmosphere, but in their study the effect was easily reverted by simply switching back to a dry mixture [30].

Effects of $CO_2$ on the CO oxidation reaction have rarely been studied. Hoflund and co-workers noted a reduced reactivity for a Au/$MnO_x$ catalyst by a factor of 2 in the presence of 16 kPa $CO_2$ (1 kPa CO, 0.5 kPa $O_2$; 55 °C) [31]. During preparation of this manuscript a study by Avgouropoulos et al. appeared, where they investigated the effects of $CO_2$ (15 kPa) and $CO_2$ (15 kPa) plus $H_2O$ (10 kPa) on the CO conversion and selectivity in the PROX reaction over a Au/$\alpha$-$Fe_2O_3$ catalyst as a function of the temperature (ca. 40–120 °C). They found that the presence of 15 kPa $CO_2$ decreased the CO conversion at a given temperature in a $H_2$-rich atmosphere markedly, while the influence on the selectivity was negligible (1 kPa CO, 1.25 kPa $O_2$, 50 kPa $H_2$) [32]. The additional presence of 10 kPa water further reduced the CO conversion, but increased the selectivity. This study did not give access, however, to reaction rates and mechanistic details. The influence of $H_2O$ on adsorbed CO was studied by in situ infrared spectroscopy (FTIR) in [33].

Finally, we have not found any data on the influence of $CO_2$ or $H_2O$ on the oxidation of $H_2$, which is equally relevant for studies of the PROX reaction.

In the following we will, after a brief description of the experimental details and procedures and of the physical properties of the catalysts, first evaluate the effect of $H_2O$ and $CO_2$ addition on the rate and selectivity for CO oxidation, determined under differential conditions. This is followed by in situ diffuse reflection infrared spectroscopy (DRIFTS) results on the evolution of the C–O stretch frequency during reaction in different reaction atmospheres, which provides information on the composition of the adlayer under reaction conditions and on the build-up and stability of by-products during the reaction. These data form the basis for mechanistic considerations. The following section is focused on the temperature dependence of the $H_2O$ and $CO_2$-induced changes in the CO oxidation rate and selectivity, giving access to the effective activation energies of the underlying reactions in the different reaction atmospheres. Finally, we evaluate the catalyst performance under realistic conditions, comparing the rates and selectivity in a realistic gas mixture containing 10 kPa $H_2O$ and 22 kPa $CO_2$ with those in idealized reformate, in the absence of $H_2O$ and $CO_2$, or in gas mixtures containing either $H_2O$ or $CO_2$.

Our data will show that for the present catalyst both coreactants cause significant, but opposite, effects on the PROX activity and selectivity and that the relative strength of the observed effects depends strongly on the reaction temperature and reactant partial pressures. Based on in situ IR data it will be shown that these effects are at least partly caused by coadsorption of $CO_2$ and/or $H_2O$/OH species on the gold particles or at the Au–oxide interface, and that the catalyst deactivation is mainly related to the build-up and accumulation of carbonate by-products. In the presence of $H_2O$ these can be transformed into thermally less stable bicarbonate species, which reduces the tendency for deactivation. Under realistic application conditions the counteracting effects of $CO_2$ and $H_2O$ addition do not completely compensate each other, and the catalyst performance is slightly inferior compared to that in idealized reformate.

## 2. Experimental

The disperse Au/$\alpha$-$Fe_2O_3$ catalysts (samples I–IV) were prepared either by deposition–precipitation or by coprecipitation from metal nitrate solutions, as described in Ref. [12]. The main physicochemical characteristics of the catalysts such as metal loading, BET surface area, the mean metal and oxide particle sizes, and the content of trace impurities, in this case mainly Na, were determined by inductively coupled plasma atom emission spectroscopy (ICP-AES), $N_2$ BET measurements (Fisons Instruments, Sorptimaic 1900) and by either X-ray diffraction (XRD) (Siemens D5000) or by transmission electron microscopy (TEM) using a Philips CM 20 microscope (200 kV). The resulting values are summarized in Table 1. Prior to the experiments, the catalysts were calcined in situ at 400 °C in a flow of 20 Nml/min of 10 kPa $O_2$ in $N_2$ for 30 min.

All measurements were conducted at atmospheric pressure under differential flow conditions. The reactant gas feed for the PROX reaction was mixed from $N_2$ (6.0), $H_2$ (5.0),

Table 1
Catalyst characterization of employed Au/$\alpha$-$Fe_2O_3$ samples after calcination

| | Preparation[a] | Au (wt%) | $Ø_{Au}$ (nm)[b] | $Ø_{Fe_2O_3}$ (nm)[c] | BET ($m^2/g$) |
|---|---|---|---|---|---|
| Sample I | DP | 2.30 | 2.3 ±0.8 | 16.5 | 63 |
| Sample II | DP | 2.55 | 2.2 ±0.8 | 18.8 | 47 |
| Sample III | DP | 2.69 | 2.7 ±1.0 | 17.3 | 40 |
| Sample IV | CP | 3.15 | 2.2 ±0.5 | 13.7 | 54 |

[a] CP, coprecipitation (pH 8–8.5; $T = 80\,°C$); DP, deposition–precipitation (pH 7.8–8.3; $T = 80/60\,°C$).

[b] Evaluated by TEM.

[c] Calculated from XRD.

2% CO (4.7) in $H_2$ (5.6), 10% $O_2$ (5.0) in $N_2$ (5.0, CO-free), and $CO_2$ (6.0), supplied by Linde, Messer Griesheim and MTI. Flow rates were between 40 and 120 Nml/min. Four different gas mixtures were used in this study, "idealized reformate," "$CO_2$-containing reformate," "$CO_2$/$H_2O$-containing reformate," and "realistic reformate." If not noted otherwise, they all contained 1 kPa CO, 1 kPa $O_2$, and 75 kPa $H_2$ in the dry part. $N_2$ (idealized reformate) or $CO_2$ (other mixtures) were used as balance gas. In the $CO_2$/$H_2O$-containing reformate, which was used as model gas still suitable, e.g., for DRIFTS measurements, the moisture content was 1.3 kPa; in the realistic reformate the moisture content was similar to that of real methanol reformate (10–15 kPa). In order to maintain differential reaction conditions, the catalysts were diluted with $\alpha$-$Al_2O_3$ powder.

Catalytic activities were measured in a tubular quartz reactor (i.d. 4 mm) with on-line gas chromatography detection (Chrompack CP9001), using two wide-bore capillary columns (Poraplot U and Molesieve 5 Å; Chrompack) and two thermal conductivity detectors (Chrompack TCD 914). The catalyst powder (approximately 100 mg) was fixed by quartz wool plugs. CO, $O_2$, and $CO_2$ signals were calibrated with calibration gas mixtures. IR spectra were recorded on a Magna 560 spectrometer (Nicolet) by adding 1250 scans (acquisition time $\sim$ 9.5 min) at a nominal resolution of 8 $cm^{-1}$ using an in situ DRIFTS cell. Details on the cell and the mirror setup are provided in Ref. [34]. Prior to the experiments background spectra were recorded on the freshly conditioned catalyst under a flow of pure nitrogen. Intensities were evaluated in Kubelka-Munk units which are linearly related to the adsorbate concentration [35]. Finally, spectral contributions from the gas phase were eliminated by subtracting corresponding spectra recorded on pure support material.

## 3. Results

First we evaluated the influence of $CO_2$ on the selective CO oxidation in long-term (1000 min) measurements, comparing the reaction rates and selectivities and their time dependence in idealized reformate and in $CO_2$-containing reformate at 80 °C. Representative results obtained on one catalyst (sample I) are presented in Fig. 1. In the presence of $CO_2$, the CO oxidation rate (upper window) is reduced roughly by a factor of 3. Moreover, the catalyst deactivation is accelerated in the $CO_2$-containing mixture. The selectivity (lower window) is decreased by 15–20%. Other than for idealized reformate, a continuous loss of selectivity is also observed with increasing time on stream. A similar behavior, reduction of the CO oxidation rate by a factor 2.5–4, faster deactivation, and significant reduction in selectivity, was noted for all Au/$\alpha$-$Fe_2O_3$ catalysts evaluated in $CO_2$-containing reformate, independent of the preparation route (coprecipitation or deposition–precipitation), Au particle size, catalyst impurities (e.g., sodium), or relative activity differences between the various samples under identical conditions (the difference in CO oxidation rate in idealized reformate between the different samples was about one order of magnitude under these conditions). Our finding of a reduced activity in the presence of $CO_2$ agrees well with the results in Ref. [32], where the addition of $CO_2$ caused a significant decrease in CO conversion over the entire temperature range investigated. In contrast to those measurements, however, we also find a considerable decrease in selectivity upon addition of $CO_2$. The origin for these differences in catalytic behavior is unclear so far, and may be related to differences in the catalyst preparation. They can not be explained by the different type of measurements in that study, using conversion measurements instead of differential flow kinetic measurements.

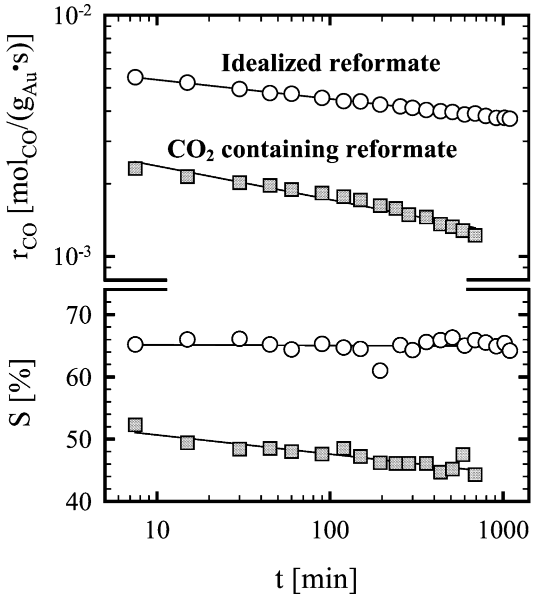

Fig. 1. Long-term measurement of the CO oxidation rate $r_{CO}$ (top) and selectivity S (bottom) during selective CO oxidation in idealized (○) and in $CO_2$-containing reformate (▨) over Au/$\alpha$-$Fe_2O_3$ (sample I) at 80 °C (1 kPa CO, 1 kPa $O_2$, 75 kPa $H_2$, balance $N_2$ or $CO_2$).

In a second set of experiments we investigated the influence of water on the selective CO oxidation. Measurements on sample I are shown in Fig. 2. In this experiment 1.3 kPa water was added to the feed after a 1200-min reaction in idealized reformate. As a result, the CO oxidation rate (upper window) increased significantly, exceeding even its initial

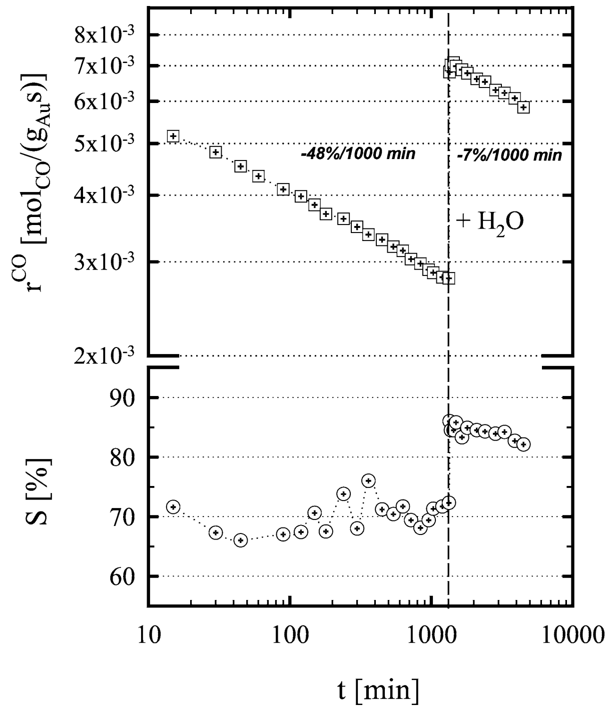

Fig. 2. CO oxidation rate $r_{co}$ (top) and selectivity S (bottom) in a "switch experiment" during selective CO oxidation in a mixture of 1 kPa CO, 1 kPa $O_2$, 75 kPa $H_2$, balance $N_2$) over Au/$\alpha$-$Fe_2O_3$ (sample I) at 80 °C: first dry mixture (idealized reformate), after 1300 min addition of 1.3 kPa $H_2O$.

rate (at $t = 15$ min) by 35%. Similar results were obtained also on other Au/$\alpha$-$Fe_2O_3$ catalysts, though in some case the addition of water had almost none or even a slightly negative effect (e.g., sample II) on the CO oxidation rate. Other observations are that in the water-containing atmosphere the deactivation is slowed down (Fig. 2, upper window) and that the selectivity is improved by ca. 15% (Fig. 2, lower window). The main reason for the enhanced selectivity is a significantly diminished $H_2$-oxidation rate in the presence of water. These effects were observed for all Au/$\alpha$-$Fe_2O_3$ samples. In several measurements the stability was enhanced to an extent that almost constant CO oxidation rates were obtained for more than 5000 min.

Despite extensive analysis (elementary analysis, TEM, BET, XRD, thermogravimetry) we could not see any significant differences in the physical properties of those catalyst samples where we noted a neutral or negative impact of water on the CO oxidation rate. This does not rule out, of course, modifications which are close to or below the detection limit of our techniques for catalyst characterization.

Next, we investigated the influence of increasing amounts of $CO_2$ (0.2–22 kPa $CO_2$) and of coadded $H_2O$ (1.3 kPa $H_2O$) by combined in situ DRIFTS and activity measurements in order to get a more detailed picture of the underlying reaction mechanism. Because of technical reasons the addition of up to 22 kPa $CO_2$ was compensated by reducing the hydrogen content rather than the balance nitrogen in these experiments. (We assume that due to its large excess a reduction from 89 to 67 kPa $H_2$ (for exact gas composition, see figure caption of Fig. 3) does not bring about significant effects.) For each data point the system was equilibrated for 30 min before taking a GC sample and recording IR spectra, so that steady-state conditions were reached, at least for the highly reversible CO adlayer. Fig. 3 (top) illustrates that with increasing partial pressure of $CO_2$ both the CO oxidation and the $H_2$ oxidation rate are reduced, with the latter being less affected (reduction by factors of 4 and 2, respectively). As a consequence, the selectivity (Fig. 3, bottom) is slowly reduced with increasing $CO_2$ content, from more than 65% in idealized reformate to about 50% in the presence of 22 kPa $CO_2$. (Note that an average base level of 0.19 kPa $CO_2$ is produced in situ by the CO oxidation reaction in idealized reformate, which was considered in the $CO_2$ partial pressures.) Finally, 1.3 kPa $H_2O$ was added to the $CO_2$-containing reformate by passing it through a bubbler (Fig. 3, black symbols). This results in a clear acceleration of the CO oxidation rate, but not of the $H_2$ oxidation rate, leading to a strong increase in selectivity.

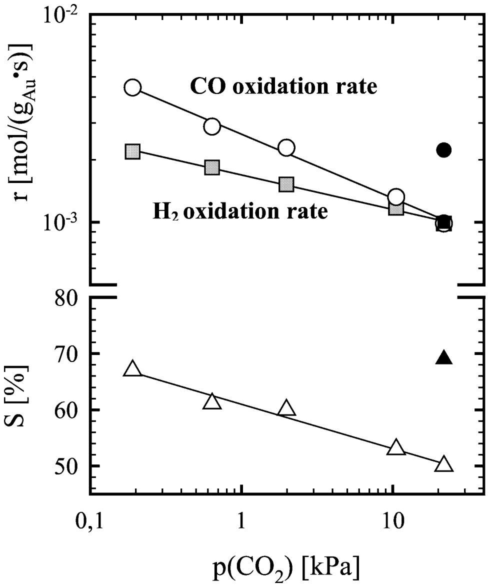

Fig. 3. Dependence of the CO (circles—top) and $H_2$ oxidation rate (squares—top) over Au/$\alpha$-$Fe_2O_3$ (sample III) and of the corresponding selectivity $S$ (triangles—bottom) on the $CO_2$ content of the reaction feed at 80 °C (1 kPa CO, 1 kPa $O_2$, 9 kPa $N_2$, up to 22 kPa $CO_2$, balance $H_2$), recorded in the in situ DRIFTS cell. Black symbols: Rates and selectivity after addition of 1.3 kPa $H_2O$ to the mixture containing 22 kPa $CO_2$.

Fig. 4 illustrates the corresponding changes in the vibrational properties of the adlayer during the above described experiments. (It should be noted that because of the very strong and dominating $CO_2$ gas-phase absorption band the spectral region between 2300 and 2400 $cm^{-1}$ is not included.) With increasing $CO_2$ partial pressure the band for linearly adsorbed $CO_{ad}$ shifts to higher wavenumbers, from 2110.5 to 2114.0 $cm^{-1}$ (Fig. 4a), while its intensity increases by almost 25% (Fig. 4b). The corresponding spectra are reproduced in Fig. 4c. If the larger CO IR-signal intensity reflected a higher CO coverage, this would contrast the usual observation for CO adsorption on Au that an increase in CO

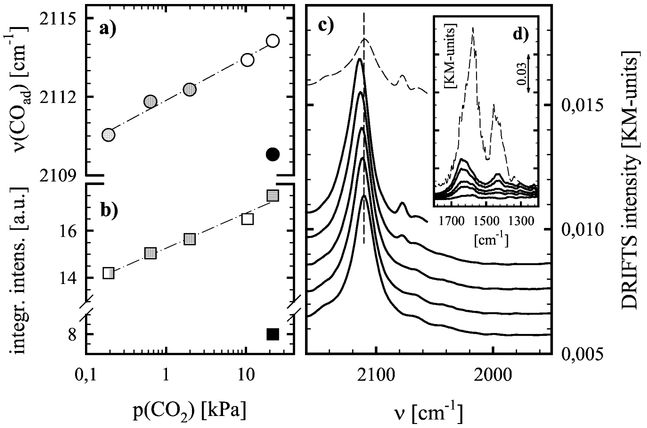

Fig. 4. Evolution of DRIFTS spectra during the PROX reaction at increasing $CO_2$ partial pressures over Au/$\alpha$-$Fe_2O_3$ (sample III) at 80 °C (1 kPa CO, 1 kPa $O_2$, 9 kPa $N_2$, up to 22 kPa $CO_2$, balance $H_2$) (the corresponding rates/selectivities are shown in Fig. 3): (a) C–O stretch frequency for linearly adsorbed $CO_{ad}$ on gold; (b) integrated IR intensity for linearly adsorbed $CO_{ad}$ on gold; (c) DRIFTS spectra of the $CO_{ad}$ region (1950–2160 $cm^{-1}$; $CO_2$ content increases upward); (d) DRIFTS spectra of the by-product region (1200–1800 $cm^{-1}$; $CO_2$ content increases upward). Black symbols/dashed lines: DRIFTS spectra after addition of 1.3 kPa $H_2O$ to the mixture containing 22 kPa $CO_2$.

coverage is concomitant with a decrease of the C–O stretch frequency [36]. Very similar effects on the position and intensity of the C–O band have been observed previously, after the admission of oxygen to a CO/$N_2$ mixture, where depending on the partial pressures of CO and $O_2$ we noted a blue shift between 3 and 7 $cm^{-1}$, together with an increase of the absolute intensity of the $CO_{ad}$ band [10], which is likely due to a coadsorbate-induced increase in the absorption cross section. (A change in catalyst reflectivity during the reaction could be ruled out as the physical orgin since we recorded single beam spectra, which were averaged subsequently and which would have shown this effect.) Considering the physical origin of the “normal” red shift of the C–O frequency with increasing coverage for CO on Au—it was attributed to the dominant interaction with the 5$\sigma$ CO orbital [36]—the C–O frequency is expected to increase with reduced electron density at the Au surface. Consequently, we suspect $CO_2$ molecules coadsorbed on the Au particles, i.e., in the vicinity of the adsorbed CO molecules, to act as an electron acceptor, reducing the electron density at the Au particle surface in their neighborhood. Possible explanations for the parallel reduction in CO oxidation activity may be steric effects (i.e., site blocking) or an altered reactivity of the surface species due to the electronic changes in the substrate. Additional effects, such as a suppression of the oxygen supply from the support material [11], especially by building up carbonate species at the gold–metal oxide interface, may contribute as well, but they are expected to affect CO and $H_2$ oxidation to the same extent and cannot account for the reduced selectivity shown in Fig. 3.

At partial pressures above 10 kPa $CO_2$ a new band evolves in the C–O stretch region at around 2075 $cm^{-1}$, which has never been observed in $CO_2$-free mixtures in our experiments. Bollinger and Vannice reported the appearance of a band at a similar position (2071 $cm^{-1}$) for CO adsorption experiments on a Au/$TiO_2$ catalyst and attributed it to CO linearly adsorbed on rutile [29], however, this cannot serve as an explanation in our case. $CO_{ad}$ bands observed in a still lower range, between 1900 and 2055 $cm^{-1}$, over a Au/$TiO_2$ catalyst sample pretreated in hydrogen, were ascribed to the adsorption of CO on small, electron-rich gold particles, which are negatively charged by interaction with the partly reduced support [37]. Since the number of oxygen vacancies on the support is not expected to increase, but rather to decrease in the presence of higher partial pressures of $CO_2$ [38], such an explanation seems unlikely for the present case. We therefore attribute this line to a $CO_{ad}$ species adsorbed on the Au particles interacting with coadsorbed, neighboring $CO_2$, without being able to specify the adsorption site or the nature of the interaction.

Coadsorption of $CO_2$ on the Au particles was already proposed in a former study by Bollinger and Vannice on Au/$TiO_2$ catalysts, who equally noted an inhibition of the CO oxidation activity upon addition of $CO_2$. Their proposal was based on the observation of shoulders at 2320 and 2378 $cm^{-1}$ for a central band around 2342 $cm^{-1}$, which they assigned to adsorbed $CO_2$ on the gold particles, while the main peak was attributed to adsorbed $CO_2$ on $TiO_2$ [29].

In order to check for carbonate- or formate-type by-products we also evaluated the spectral region between 1200 and 1800 $cm^{-1}$, i.e., the region typical for these by-products [24,35]. The resulting spectra are displayed in Fig. 4d. They show a number of absorption lines, which grow in intensity with increasing $CO_2$ partial pressure. The most prominent peaks and shoulders are at 1220, 1305, 1430–1440, 1610, and 1640 $cm^{-1}$, which are assigned to various types of carbonate and probably also carboxylate species (e.g., [24,29,35,39]). Due to the contradictory interpretations in the literature and since there are only few data on $Fe_2O_3$ [39] supports we refrained from a more detailed assignment (except for the well distinguishable bicarbonate species, see below).

After the addition of water (1.3 kPa $H_2O$) to the $CO_2$-containing reformate ($CO_2$/$H_2O$-containing reformate) the $CO_2$-induced effects are reversed. The $CO_{ad}$ band shifts to lower wavenumbers and its intensity is reduced to less than half of its original value (Figs. 4a–c, black symbols and dashed lines, respectively). The peak at 2075 $cm^{-1}$ remains, indicating that adsorbed $CO_2$ is still present under these conditions and has not been removed by reaction with water, e.g., by forming bicarbonate species. Consequently, the $H_2O$-induced red-shift of the C–O stretch frequency and the strongly reduced IR intensity must be explained in terms of coadsorbed electron-rich $H_2O_{ad}$ or $OH_{ad}$ species on the gold surface (or at the interface region).

The intensity in the by-product region between 1200 and 1800 $cm^{-1}$ is not only strongly enhanced, but also the peak positions are changed. The strongest bands and shoulders appear now at 1340, 1400–1460, 1580, and ∼ 1650 $cm^{-1}$ (Fig. 4d). While the bands observed under dry conditions were assigned carbonate and carboxylate species, the large bands in the presence of water are tentatively related to bicarbonate species (e.g., [25,40], see also next experiment).

For closer inspection of the water influence on these by-products a second set of in situ DRIFTS experiments was performed. First, by-products were accumulated for 1 h of CO oxidation (1 kPa CO, 1 kPa $O_2$, balance $N_2$, 80 °C). Subsequently, the catalyst was purged in different atmospheres (see below) for an additional 30 min at the reaction temperature. In each experiment the transmittance spectrum taken at the end of the purging step was divided by the transmittance spectrum acquired at the end of the accumulation step. This results in normalized spectra, where species that have been removed during the purging procedure are identified by upward showing bands, while downward showing bands indicate newly formed species (Fig. 5). For purging in pure nitrogen (spectrum a) or in either $O_2/N_2$ mixtures (10 kPa $O_2$ in $N_2$) (spectrum b) or in $H_2/N_2$ mixtures (75 kPa $H_2$ in $N_2$) (spectrum c) the intensity of the by-products formed during reaction is reduced by similar amounts, and no new bands are found. This is different in an atmosphere containing both $H_2$ and $O_2$ (75 kPa $H_2$ + 1 kPa $O_2$ in $N_2$, spectrum d), where water is being produced in situ at the catalyst surface (From experimental reasons this experiment is favorable compared to adding water vapor to the feed gas, since it eliminates the impairing interference from the rotational gas-phase spectrum of water introduced via the gas feed). In this case the former by-product bands are reduced to a much larger extent, and in addition new bands appear at 1455, 1660, and 3620 $cm^{-1}$ (marked by arrows), along with another small peak at 1775 $cm^{-1}$. As had been discussed before, the first two lines are assigned to bicarbonates, and the line at 3620 is typical for the O–H stretching vibration in bicarbonates, e.g., in bicarbonates on rutile [29].

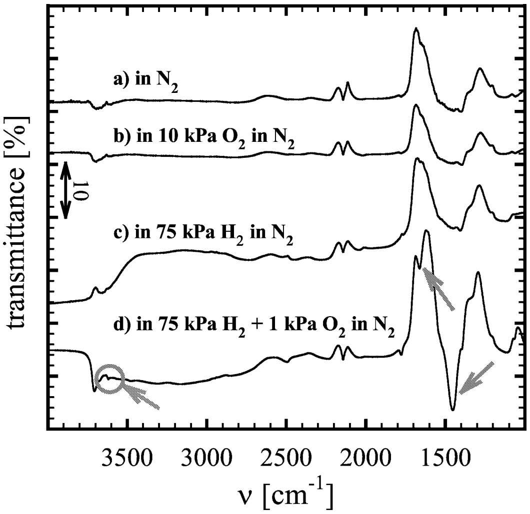

Fig. 5. Variation of adsorbed by-products during purging of a by-product containing Au/α-$Fe_2O_3$ catalyst (sample IV) in different gas mixtures (80 °C; for 30 min), after accumulation of by-products for 1 h of CO oxidation (1 kPa CO, 1 kPa $O_2$, balance $N_2$) at 80 °C. The spectra were produced by dividing the transmittance spectra recorded after the purging step by the transmittance spectra taken at the end of the accumulation step. Upward showing bands indicate disappeared species, while downward showing band are assigned to newly formed species on the catalyst surface.

First of all these results indicate that, first, keeping the catalyst in a non-reactive atmosphere at 80 °C leads to a slow thermal decomposition of the carbonate by-products formed during CO oxidation under dry conditions. Second, the presence of water at the catalyst surface does not just add additional by-products on top of the already existing ones, but results in their enhanced decomposition compared to the unreactive atmosphere. We attribute the faster removal of the carbonate by-products to a reactive conversion into bicarbonate species. The latter in turn are known to be less stable toward thermal decomposition than the original carbonate [41].

The build-up of carbonate species has been identified as a main source for the deactivation of gold catalysts during selective CO oxidation, most likely by blocking the Au–metal oxide interface [12]. The above experiments showed that water mitigates the deactivation during selective CO oxidation. Even the activity of a completely deactivated Au/α-$Fe_2O_3$ catalyst (during CO oxidation in pure $N_2$) could be largely regenerated by switching to a water-containing atmosphere [18]. Similar effects of catalyst regeneration in the presence of water were also reported by Costello et al. for a Au/γ-$Al_2O_3$ sample [15].

It is interesting to note that the beneficial effect of water is observed only for the CO oxidation, but not for the competing $H_2$ oxidation (Fig. 3) which shows the inhibiting effect on the latter reaction, that was held responsible for the increasing selectivities in the presence of water in Fig. 2.

All of the above studies were conducted at a reaction temperature of 80 °C. In the following experiments we investigated the temperature dependence of the PROX performance in idealized reformate, in $CO_2$-containing reformate, and in $CO_2/H_2O$-containing reformate in a temperature range between 40 and 120 °C. The data are arranged in Arrhenius-type diagrams in Fig. 6. All values displayed represent an average of 2–4 independent measurements. Standard deviations in the resulting activation energies are calculated to be around ±5 kJ/mol for CO oxidation (Fig. 6a) and ±7 kJ/mol for $H_2$ oxidation (Fig. 6b). The data show that, although the CO oxidation rate in $CO_2$-containing reformate is significantly lower than in idealized reformate, its temperature dependence remains rather similar, yielding activation energies of around 30 kJ/mol for both reaction atmospheres (Fig. 6a). When water is added to the $CO_2$-containing reformate ($CO_2/H_2O$-containing reformate), the temperature dependence turns out to be less pronounced. While at low temperatures (40 °C) the initial CO oxidation rate is similar to that in idealized reformate, it approaches the lower rate in $CO_2$-containing reformate at higher temperatures. This leads to a lower activation barrier of around 20 kJ/mol in $CO_2/H_2O$-containing reformate under the present reaction

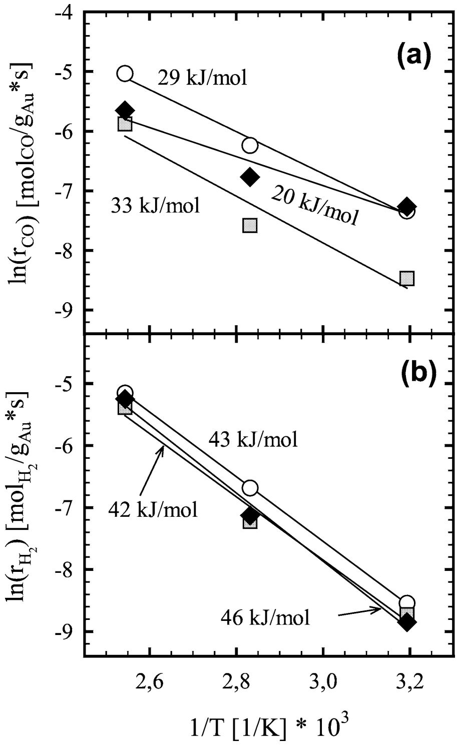

Fig. 6. Arrhenius diagram for the CO oxidation rate (a) and the $H_2$ oxidation rate (b) during selective CO oxidation (1 kPa CO, 1 kPa $O_2$, 75 kPa $H_2$, balance $N_2$ or $CO_2$) over Au/ $\alpha$-$Fe_2O_3$ (sample II) in idealized reformate (○), in $CO_2$-containing reformate (▨), and in $CO_2$/$H_2O$-containing reformate (◆; 1.3 kPa $H_2O$).

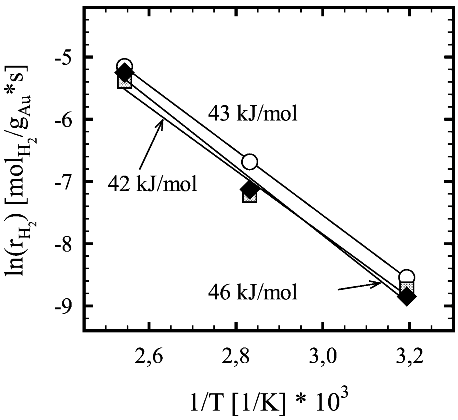

Fig. 7. Temperature dependence for the selectivity during selective CO oxidation (1 kPa CO, 1 kPa $O_2$, 75 kPa $H_2$, balance $N_2$ or $CO_2$) over Au/$\alpha$-$Fe_2O_3$ (sample II) in idealized reformate (○), in $CO_2$-containing reformate (▨), and in $CO_2$/$H_2O$-containing reformate (◆; 1.3 kPa $H_2O$).

conditions. Fig. 6b shows the corresponding data for the competing $H_2$ oxidation in the three different atmospheres. The effects of $CO_2$ and water on the activation barrier of the $H_2$ oxidation are much smaller than for the CO oxidation reaction, resulting in activation energies of around 45 kJ/mol for all three reaction atmospheres.

The temperature dependence of the selectivity in the different feed mixtures derived from the above data is shown in Fig. 7. The selectivity behavior in the $CO_2$-containing mixture parallels the trend in idealized reformate, but is 15–20% lower. The additional presence of water improves the selectivity only for lower temperatures, while for 120 °C almost no effect is visible.

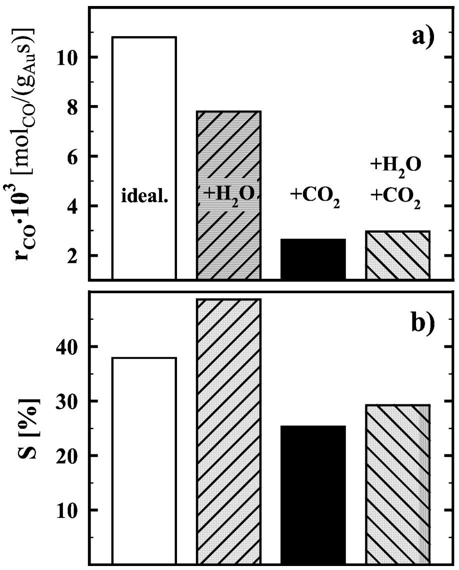

Fig. 8. Rate (a) and selectivity (b) for the selective CO oxidation over Au/$\alpha$-$Fe_2O_3$ (sample IV) at 80 °C in different reaction feed mixtures (0.1 kPa CO, 0.1 kPa $O_2$, 75 kPa $H_2$, and balance $N_2$ or $CO_2$; data taken after 2 h on stream): column 1 (left): idealized reformate; column 2 (left middle): idealized reformate mixed with 12 kPa $H_2O$; column 3 (right middle): $CO_2$-containing reformate; column 4 (right): $CO_2$-containing reformate mixed with 10 kPa $H_2O$ (realistic reformate).

In order to evaluate effects of realistic water concentrations—water concentrations in real feed gas from a methanol reformer unit are much higher, around 10–15%—we also investigated the influence of $H_2O$ and $CO_2$/$H_2O$ additions on the PROX reaction over Au/$\alpha$-$Fe_2O_3$ catalysts at 80 °C at these higher water levels. The relative excess of the feed impurities was further increased in these measurements by reducing the partial pressures of CO and $O_2$ to 0.1 kPa. Rates and selectivities determined in measurements on sample IV under these conditions are shown in the bar diagram in Fig. 8. (Note that because of the much lower CO and $O_2$ partial pressures the CO oxidation rates and selectivities are different from those in Fig. 1, in agreement with previous findings reported in Ref. [9].)

The resulting effects are very similar to what was observed before at lower water concentrations. After adding 12 kPa water to the idealized reformate the CO oxidation rate decreases slightly compared to idealized reformate and the selectivity is enhanced by ca. 10% (columns 1 and 2). For $CO_2$-containing reformate (25 kPa $CO_2$) the CO oxidation rate decreases significantly, to about 20% of that in idealized reformate, and the selectivity decreases by about 30% (columns 1 and 3). Adding 10 kPa of water to the $CO_2$-containing reformate, the negative effects of $CO_2$ are reversed (compare columns 3 and 4). However, the original CO oxidation rate and selectivity (in idealized reformate) are not fully restored in the realistic reformate mixture. For all mixtures the observed effects do not exceed those observed before at lower water partial pressures and more CO and oxygen present.

These experiments, which were conducted as close as possible to realistic conditions, show that under these conditions the effects of $CO_2$ and $H_2O$ only partly compensate each other. Especially the CO oxidation rate remains significantly lower compared to the rate in idealized reformate.

## 4. Conclusions

We have shown that both water and $CO_2$ have pronounced and diametrical effects on the preferential CO oxidation in $H_2$-rich gases (PROX reaction) over $Au/Fe_2O_3$ catalysts at 80 °C. Addition of water (1 kPa) usually led to a slight increase of the CO oxidation. The rate of the competing $H_2$ oxidation, on the other hand, is reduced, resulting in an average increase in selectivity by 15%. Finally, water addition reduces the catalyst deactivation, which is caused by formation of carbonates generated, e.g., during CO oxidation in pure $N_2$ or in dry $CO_2$-containing reformate. We explain this by transformation of carbonates into thermally less stable bicarbonate species.

Addition of $CO_2$ leads to opposite effects. At 80 °C it decreases the CO oxidation rate, by about a factor of 2–4, depending on the partial pressure, and also the selectivity, by about 15%. Based on the blue shift of the C–O stretch frequency at 2110 $cm^{-1}$ with increasing $CO_2$ pressure this is explained by coadsorption of $CO_2$ on the gold particles or at the gold–metal oxide interface. The effect of $CO_2$ is almost independent of the temperature, reflecting similar activation energies in idealized reformate and in $CO_2$-containing reformate for both CO oxidation and $H_2$ oxidation. In addition, the deactivation is enhanced due to faster carbonate formation, and also the selectivity decreases steadily with time, by about 5–7% over 1000 min.

The effect of water is slightly different, when it is not added to idealized reformate, but to a $CO_2$-containing feed. The CO oxidation rate in idealized reformate is partly restored, while the $H_2$ oxidation rate, which has been lowered by the presence of $CO_2$, remains at this lower level. This results in a significant increase in selectivity compared to the PROX reaction in dry $CO_2$-containing reformate. A red shift for the linearly adsorbed CO under conditions of a $CO_2/H_2O$-containing reformate indicates that water (or hydroxy species) coadsorbs on the gold particles or at the Au–oxide interface. The effects of water addition are very sensitive to the reaction temperature. They are very prominent at a reaction temperature of 40 °C, while at 120 °C hardly any differences are observed. This is reflected by the lower activation energy for CO oxidation under these conditions, which is reduced by one-third, from about 30 to 20 kJ/mol. On the other hand, the $H_2$ oxidation rate and its temperature dependence are hardly affected—the activation energy remains at the value obtained also in ideal and $CO_2$-containing reformate of about 45 kJ/mol, which results in the observed decay of the selectivity with temperature, from a value characteristic of idealized reformate at 40 °C (85%) to one typical for $CO_2$-containing reformate (40%) at 120 °C.

The deactivation is slowed down or even reversed by the transformation of carbonate species into thermally less stable bicarbonate species, which are decomposed at a higher rate than carbonates.

Under realistic conditions, at higher $H_2O$ partial pressures, the trends are similar to those observed in $CO_2/H_2O$-containing reformate. Addition of water leads to both an increased CO oxidation rate and an increased selectivity compared to $CO_2$-containing reformate, partly compensating the negative influence of $CO_2$ on the preferential CO oxidation over $Au/\alpha\text{-}Fe_2O_3$ when compared to $CO_2$-free gas mixtures. The values obtained in idealized reformate, however, are not fully reached. The trends found in these measurements are in good agreement with those determined in conversion measurements in Ref. [32].

The above data help to better estimate the applicability of $Au/\alpha\text{-}Fe_2O_3$ catalysts for the CO removal from methanol reformer feed gas streams for PEFCs. Although these catalysts do not fully reach the activity/selectivity found under idealized conditions, they are nevertheless promising candidates for a technical application.

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